공학석사학위논문

Stabilization and reduction in bioaccessibility of As-contaminated soil through *in situ* co-precipitation of amorphous Fe oxides

비정질 철산화물 원위치 공침을 통한 비소오염토양 안정화 및 생물학적접근성 저감

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박진희의 석사 학위논문을 인준함

2019 년 8 월

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Abstract

Stabilization and reduction in bioaccessibility of As-contaminated soil through *in situ* co-precipitation of amorphous Fe oxides

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This study used *in situ* amorphous Fe oxide synthesis to form Fe-As co-precipitates with high resistance to chemical extraction in As-contaminated soil. Fe oxide was formed by injecting 2% soil mass of iron nitrate and 30% water, and adjusting to neutral pH. Effectiveness was assessed using a five-step sequential extraction and solubility/bioavailability research consortium (SBRC) method. The five-step sequential extraction demonstrated that >50% of extractable As [i.e., sum of SO_4^{2-} and PO_4^{3-} extractable As] in original soil samples was converted to less extractable fractions [i.e., oxalate extractable As] after *in situ* co-precipitation at an L/S ratio of 0.3. Consistent with the solvent extraction results, the SBRC revealed decreased bioaccessibility. *In situ* stabilization dramatically decreased bioaccessibility from 71.6 to 33.5% and 64.9 to 26.3% in soil samples. X-ray absorption near edge structure (XANES) with linear

combination fitting (LCF) confirmed the formation of schwertmannite or ferrihydrite, indicating amorphous Fe oxide precipitation. Aging confirmed that As bound to amorphous Fe oxides decreased but crystalline Fe oxides increased (i.e., transformation of amorphous Fe oxides into more stable crystalline Fe oxides). Consequently, bioaccessibility of stabilized soils was noticeably alleviated. Such increase was consistent with the XANES results showing increased goethite. Overall, *in situ* co-precipitation of amorphous Fe oxides using As effectively reduced bioaccessibility of As-contaminated soil long-term.

Also, the effects of the neutralizing agent on bioaccessibility of As(V) was investigated. SBRC assessed bioaccessibility of Fe oxides synthesized using NaOH or CaO. As the result, bioaccessibility was much lower in that case of being synthesized with NaOH than CaO. Such results were consistent with that Ca-Fe arsenate minerals have high bioaccessibility in previous study. In order to confirm the effects of neutralizing agents, soil sample pH was adjusted to neutral levels using CaO or NaOH when *in situ* stabilization applied. After stabilization, the fraction of non-specifically and specifically sorbed As(V) was remarkably decreased in both samples. On the other hand, As(V) bound to amorphous Fe oxides increased from 61.2% to 85.4% and to 85.5% in CaO treated soil and NaOH treated soil, respectively. Bioaccessibility was remarkably decreased in the soil sample used NaOH as a neutralizing agent, but not changed significantly when used CaO. Besides, XANES-LCF confirmed that arseniosiderite, a kind of calcium-iron arsenate, was formed in stabilized soils when CaO used as neutralizing agent. It is reported that labile calcium on neutral pH might form calcium-iron arsenate which has high

bioaccessibility. Therefore, it is necessary to use appropriate neutralizing agents to reduce bioaccessibility when applying *in situ* stabilization through co-precipitation of Fe oxides.

Keywords: *in situ* stabilization, amorphous Fe oxides, bioaccessibility, neutralizing agent, X-ray absorption near edge structure, aging

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1. Introduction

1.1 Background

Contamination of soil with pentavalent inorganic arsenate [iAs(Ⅴ)] occurs widely around human developments. The International Agency for Research on Cancer considers As a carcinogen (Straif et al., 2009) and environmental As may have harmful human health effects by contaminating surface water, groundwater, or crops (Jeon et al. 2008). Therefore, contaminated soil should be appropriately treated to remove arsenic and alleviate the risk to human health. In general, aggressive remediation technology such as soil washing have been often used to remove heavy metals and metalloids in soil (Legiec et al. 1997); however, such harsh *ex situ* treatments may cause ecosystem disturbances because of direct excavation of soil and excessive elimination of soil constituents including organic matter, inorganic nutrients such as nitrogen and phosphate, and essential trace elements (Khalid et al. 2017). In contrast, *in situ* methods chemically stabilize the compound in question in the soil with the addition of suitable stabilizing agents that induce sorption, co-precipitation, or both (Chlopecka and Adriano 1996). These *in situ* techniques are less environmentally damaging and are especially useful where *ex situ* treatments are difficult to apply (An et al. 2019). However, while As(V) can be chemically stabilized *in situ*, it is still environmentally present and may have toxic effects on humans even in the stabilized state. A key exposure route for As(V)-contaminated soil is incidental soil ingestion, caused by the hand-to-mouth activities pathway of

children (Markus and McBratney 2001) and, so, developing tools to minimize oral bioaccessibility of As(V) is a public health concern.

The stabilization of As(V) in soil with various sorbents has been studied for several decades, with Fe oxides emerging as one of the most effective sorbents (Giménez et al. 2007). The positively charged surface of Fe oxides can combine with As(V) (i.e., $HAsO_4^{2-}$ and H_2AsO^{4-}) through the formation of outer- or inner-sphere complexes (Catalano et al. 2008) and, thereby, Fe-based sorbents effectively induce adsorption of As(V) in the soil (Aredes et al. 2012). In fact, the following two different processes govern the reduction in bioavailability of As(V) using Fe oxides. 1. When Fe compounds are added to As(V) and Fe oxides form, in situ co-precipitation occurs. 2. When As(V) is added to already formed Fe oxides, adsorption occurs (Crawford et al. 1993). However, it is known that As(V) adsorbed on Fe oxides has higher oral bioaccessibility than that of co-precipitates (Jeong et al. 2017). Recent study reported that heavy metals can be removed efficiently through co-precipitation with Fe oxides. Dissolved heavy metals in acid mine drainage (AMD) are co-precipitated with Fe oxides through oxidation and neutralization of the AMD. Such co-precipitation occurs when Fe-hydroxide sulfate mineral are precipitated by oxidation of dissolved sulfate and Fe^{2+} (España et al. 2006). In synthetic AMD, As(V) was removed 99% by Fe oxides co-precipitation at Fe/As mole ratio of 5 (Wang et al. 2003), but a higher molar ratio (e.g., Fe/As mole ratio of 33) was required when As(V) was adsorbed to the preformed Fe oxides (Raven et al. 1998). When such co-precipitation happens to As-contaminated soil, As(V) would exhibit very low bioaccessibility and thus effectively control the potential risk at the contaminated site.

Therefore, the aim of this study was to develop an *in situ* stabilization strategy for As-contaminated soils that alleviates oral bioaccessibility of As(V) in soil by the co-precipitation of amorphous Fe oxides. Experimentally, *in situ* formation of Fe oxides was performed in As-contaminated soil to induce co-precipitation between Fe oxides and soil As(V), and a chemical extraction method named solubility/bioavailability research consortium (SBRC), as a surrogate for bioaccessibility, was used with the co-precipitates. Also, in the process of *in situ* stabilization, pH was adjusted using two different type of neutralizing agents and compared the effects on bioaccessibility. X-ray absorption near edge structure (XANES) was conducted with the aid of linear combination fitting (LCF) to investigate the alteration in types of Fe oxides involved in the reduced chemical extractability of As(V).

1.2 Research objectives

The objective of this research is to stabilize and reduce bioaccessibility of As-contaminated soil through co-precipitation of amorphous Fe oxides. The detailed purpose is as follows.

(1) This study aims co-precipitation of amorphous Fe oxides with As(V) as stabilization method to reduce bioaccessibility and comparison with adsorption.

(2) This study aims to form amorphous Fe oxides by injecting iron nitrate and neutralizing agent into soil, and to lower bioaccessibility through co-precipitation with As(V).

(3) Ths study aims to confirm the effects of neutralizing agents on bioaccessibility and the formation of Fe oxides.

1.3 Research area

In this study, co-precipitation of As(V) was carried out to reduce bioaccessibility of As(V) in soil. Before and after *in situ* stabilization, chemical extractability of soil arsenic was compared. Also, XANES analysis was performed to soil samples. The details and contents are as follows.

(1) Characterization of co-precipitation

Co-precipitated As(V) with Fe oxides was compared to adsorbed As(V) on Fe oxides. Based on this, it was proved that As(V) can be co-precipiated with Fe oxides by occlusion.

(2) Effects of *in situ* stabilization

Bioaccessibility and fractionation of soil As(V) were compared before and after *in situ* stabilization. Long-term effects of stabilization was also investigated. Besides, XANES analysis was performed to identify the type of Fe oxides produced after stabilization.

(3) Effects of neutralizing agents

Two kinds of neutralizing agents were used to control pH in the stabilization process for As-contaminated soil. It was confirmed whether the neutralization agents affect bioaccessibility of As(V) and

the kind of Fe oxides formed.

2. Literature review

2.1 Arsenic (As)

2.1.1 Background

Arsenic (As) is widely found in the nature such as minerals, rocks, sediments and soils. It is the 20th most widely distributed element among the earth's surface constituents and may exist as a different species depending on pH and oxidation-reduction conditions (Cullen and Reimer 1989). In general, it mainly exists as arsenite (As(Ⅲ)) under reducing conditions, while arsenate (As(Ⅴ)) under oxidizing conditions. In previous studies, it is known that As(Ⅲ) has higher mobility and 25-60 times of toxicity than As(Ⅴ) due to lower affinity to a mineral surface. These compounds are exposed to nature and humans through a variety of routes including industrial wastewater, chemical alloys, pesticides, combustion of fossil fuels, and mining operations (Chou and Harper 2007).

Soil contamination with As(V) occurs with industrial activities such as mining and smelter, and it exposed to human bodies and ecosystems via soil, groundwater and crops (Jeon et al. 2008).

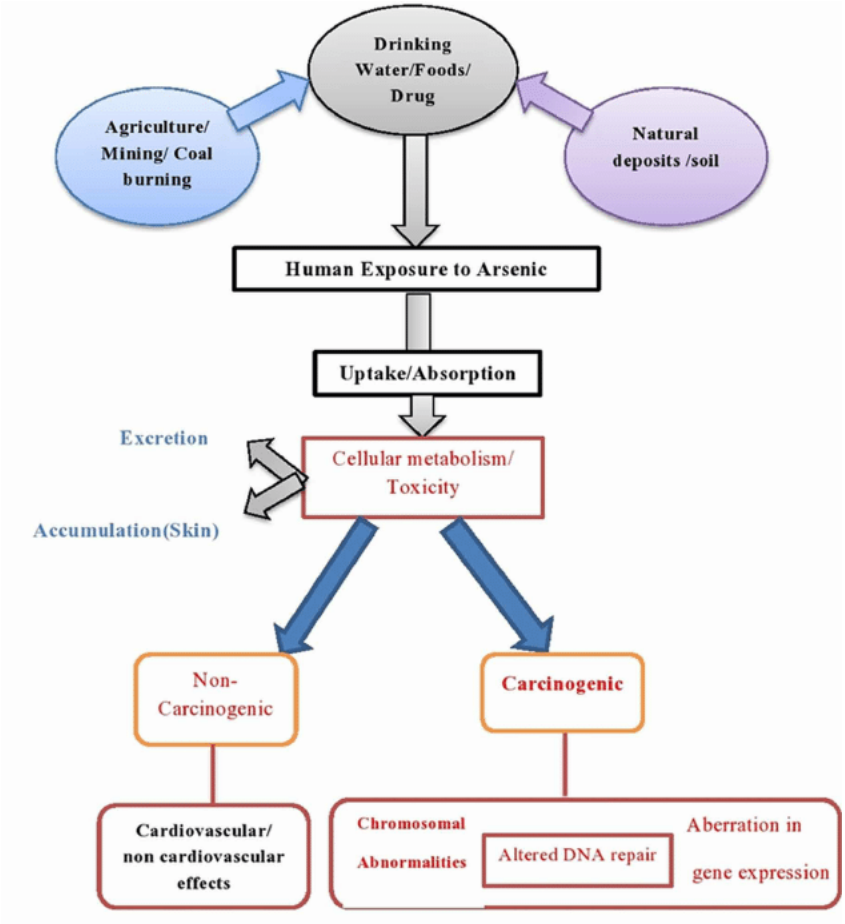

Fig 2.1 Toxic effects of arsenic and its route for human exposure (Sultana et al. 2015)

2.1.2 As(V) fractionation in soil

Soil arsenic exists in various forms. First, the most easily extractable As(V) is the form weakly sorbed to soil particles, and this is exchanged by competitive ions such as sulfate or phosphate. Among them, phosphate is known as the most effective exchangeable ion due to its similar chemical properties with As(V). The soil arsenic also presents in the form of co-precipitated with or adsorbed onto Fe/Al/Mn oxides. Since the point of zero charge (PZC) of the Fe oxides found in the soil is from 7-10 (e.g. crystalline Fe oxides 9.2, amorphous Fe oxides 7.8), it is positively charged in general environment and can combine with arsenic in soil (Schwertmann and Cornell 2000). The most stable form is As(V) associated with the minerals such as arsenopyrite (FeAsS), realgar (AsS), and orpiment (As_2S_3). This is not only less likely to be leached out of the environment, but also has no bioaccessibility.

2.2 *In situ* stabilization

2.2.1 Background

An aggressive remediation such as soil washing, which removes contaminates, has been mainly applied to the heavy metal-contaminated soils (Legiec et al. 1997). However, such *ex situ* is an expensive and destructive method in that it requires direct excavation of contaminated soils and sites. Therefore, *in situ* method such as solidification/stabilization can be used as alternatives to be

cost-effective and sustainable method. These methods prevent contaminants exposure from the soil without removal of contaminants. Among them, stabilization makes the contaminants to more chemically stable form with addition of binding agents, which makes the contaminants less likely to be released into the environment (Knox et al. 2000). Besides, stabilized sites can be re-used unlike when solidification method is applied.

Fig 2.2 Example of procedure for application of stabilizing agents in As-contaminated soil (An et al. 2019)

2.2.2 Fe oxides

Various stabilizing agents to As-contaminated soil has been studied for several decades, with Fe oxides emerging as one of the effective sorbent. It is known that Fe oxides is abundant in nature and non-expensive. The positively charged surface of Fe oxides can combine with As(V) (i.e., $HAsO_4^{2-}$ and H_2AsO^{4-}) through the formation of outer- or inner-sphere complexes (Schwertmann and Cornell 2000). However, As(V) is known to be removed more effectively by co-precipitation with Fe oxides. Co-precipitation occurs when Fe oxides was formed in the presence of As(V), while adsorption occurs when As(V) is added to pre-formed Fe oxides (Crawford et al. 1993). However, it is not clear to differentiate co-precipitation and adsorption in the nature due to variable environmental conditions (Park et al. 2016).

2.3. Bioaccessibility

2.3.1 Background

As(V) has been regarded to be harmful because of carcinogenetic and nuerological effects on humans (Rossman 2003). Such risk to human may occur through various pathways, especially main route which has the high risk is incidental soil ingestion via hand-to-mouth activities. When this happens, soil As(V) can be absorbed through the gastrointestinal phase and transferred to tissues via the systemic circulation system (Juhasz et al. 2007). However, assessing this through total concentration is not appropriate due to

concern that bioaccessible concentration could be overestimated. Actually, bioaccessible concentration is not proportional to total concentration of metals, but more associated with the chemical characteristics of these metals (Liang et al. 2016).

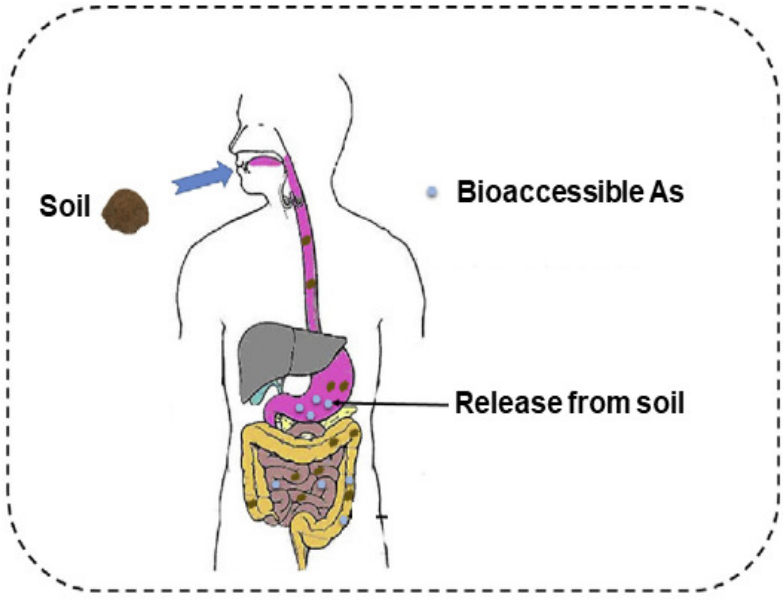

Fig 2.3. Soil As(V) transferred into gastric phase by soil injection (Modified Wang et al. 2018)

2.3.2 *In vitro* test

Bioaccessibility of As(V) in soil has been mainly determined using *in vivo* tests on animals, but these methods has disadvantages in respect to high costs and time consuming, so *in vitro* tests has been developed as the alternatives. *In vitro* test mimics the human digestion systems to estimate the fraction that is soluble and absorbed in the gastrointestinal phase. It is reported that various methods such as Solubility/Bioavailability Research Consortium (SBRC) method (Kelley et al. 2002), the Physiologically Based Extraction Test (PBET) method (Ruby et al., 1996), and the In Vitro Gastrointestinal (IVG) method (Rodriguez et al. 1999) has been developed.

Also, these methods have also been reported to be useful in assessing the risk of heavy metals for the human body. The relative bioavailability (RBA) obtained from *in vitro* bioaccessibility (IVBA) and *in vivo* tests has been known to have high correlation. For example, Bradham et al. (2011) found a strong correlation between bioaccessibility of As obtained from the gastric phase of SBRC method and that of *in vivo* test. In particular, SBRC estimates As-bioaccessibility conservatively than other methods due to its much lower pH which simulates gastric phase.

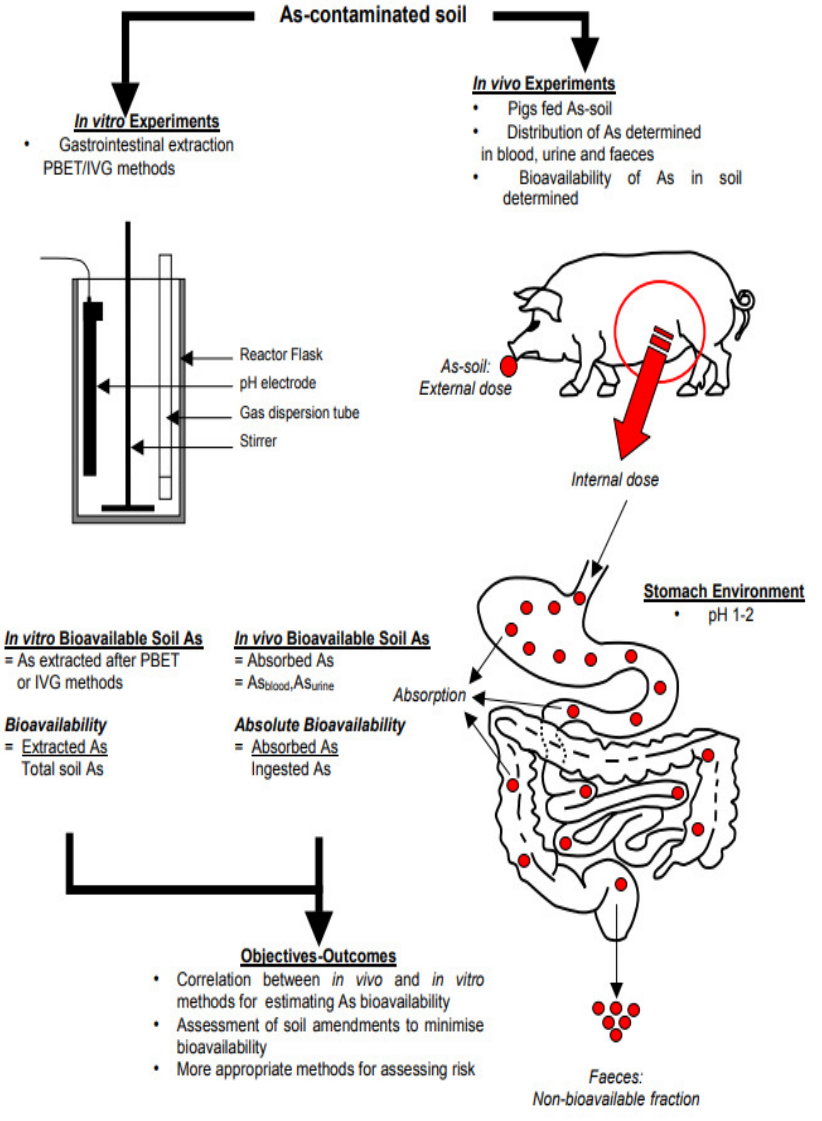

Fig 2.4. Schematic diagram of *in vivo* and *in vitro* test (Juhasz 2003)

3. Materials and method

3.1 Materials

3.1.1 Preparation of soil samples

Soil samples were air-dried and passed through a 2 mm sieve. The samples were artificially contaminated with As(V) (sodium arsenate dibasic heptahydrate, $Na_2HAsO_4 \cdot 7H_2O$, Fluka, +98.0% purity). To compare the effects of aging, two soil samples (soil A and B) before and after *in situ* stabilization were aged for 5 months at room temperature. The physicochemical properties of the soil include pH, texture, organic matter content (OM), cation exchange capacity (CEC), and Fe/Al oxide content and are summarized in Table 1. The properties were diverse: pH 3.8-7.6, organic matter content 1.2-8.9%, Fe oxide concentration 2,527-11,685 mg/kg, and Al oxide concentration 205-726 mg/kg.

Table 3.1 Properties of the soil samples used in this study

Label	Land use	Soil texture	pH (1:5)	OC (%)	CEC (cmol/kg)	Fe oxides (mg/kg)	Al oxides (mg/kg)
A	forest soil	sandy loam	5.9	8.9	27.3	2527	280
B			7.6	4.4	16.3	2698	205
C			3.8	1.2	10.61	11685	726

3.2 Method

3.2.1 Total As(V) concentration

Total As(V) concentration of soil samples was analyzed according to EPA 3052 method (Kingston and Walter 1988). To decompose the soil sample, HNO_3, HF, H_2O_2 and dH_2O (9:3:1:1, v/v/v/v) were added to 1 g of soil and heated in the microwave for 5.5 minutes to 180℃ and maintained for 9.5 minutes. After cooling at room temperature, the supernatant fluids was filtered using a 0.45 μm GHP filter and diluted to 25mL with dH_2O and analyzed by an inductively coupled plasma optical emission spectrometer (ICP-OES, iCAP7400 Series, Thermo Scientific, USA)

3.2.2 Five step sequential extraction

To investigate the chemical fractionation of As(V) in soil, five step sequential extraction was performed on the soil samples (Wenzel et al. 2001). For all procedures, the solid to solution ratio (mL/g) was 25. First, 0.05 M $(NH_4)_2SO_4$ was used to extract non-specifically bound As(V) (F1), and the reaction time was 4 h. Then, 0.05 M $(NH_4)H_2PO_4$ was added, and a reaction time of 16 h was allowed for extraction of specifically bound As(V) (F2). To release As(V) bound to amorphous Fe oxides (F3), 0.2 M of NH_4-oxalate buffer (pH 3.25) was added to the samples and allowed to react at room temperature for 4 h in the dark. To extract As(V) bound crystalline Fe oxides (F4), the samples were treated with 0.2 M NH_4-oxalate buffer and 0.1 M ascorbic acid (pH 3.25) for 30 min at 96 ± 3 °C. Between the

sequential procedure, each sample was centrifuged at 14,000 g for 10 min (IECMULTI-RF, Thermo scientific, USA) and filtered through a 0.45-μm GHP filter for analysis. Residual As(V) (F5) was extracted according to USEPA 3052 method. The As(V) concentration of the sample was analyzed using an ICP-OES and the total As(V) concentration was estimated by summing the concentration of total fraction.

Table 3.2 Extraction procedures of Wenzel's sequential extraction procedure and USEPA 3052 method

Step	Chemical form	Extractant	Extraction methods
1	Non-specifically bound As(V)	0.05 M $(NH_4)_2SO_4$	S/L ratio = 1:25 4h shaking, 20℃
2	Specifically bound As(V)	0.05 M $(NH_4)H_2PO_4$	S/L ratio = 1:25 16h shaking, 20℃
3	As(V) bound to amorphous Fe/Al oxides	0.2 M NH_4-oxalate buffer; pH 3.25	S/L ratio = 1:25 4h shaking in the dark, 20℃
4	As(V) bound to crystalline Fe/Al oxides	0.2 M NH_4-oxalate buffer + 0.1 M ascorbic acid ; pH 3.25	S/L ratio = 1:25 30min in a oil bath at 96±3℃
5	Residual	HNO_3 : HF : H_2O_2: dH_2O (9:3:1:1, v/v/v/v)	Microwave digestion

3.2.3 Assessment of bioaccessibility

The SBRC method (Kelley et al. 2002) was used to determine bioaccessibility of soil arsenic before and after *in situ* stabilization. It evaluates bioaccessibility by quantifying the amount of As(V) absorbed into the human body. To simulate gastric fluid conditions, 1 g of the soil sample (below 150 μm) was mixed with 100 mL of 0.4 M glycine buffer solution titrated to pH 1.5 ± 0.05 with HCl. Samples were then placed in a high-density polyethylene bottle and stirred at 37°C for 1 h. To determine As(V) concentration, supernatant fluids were filtered using a 0.45 μm GHP filter and analyzed using an ICP-OES

3.2.4 X-ray diffraction (XRD) analysis

The powder XRD patterns were collected on a D8 ADVANCE with DAVINCI with design diffractometer from Bruker AXS (Karlsruhe, Germany) with graphite monochromated $CuK_{\alpha 1}$ radiation. The powder were scanned from 5 to 90° 2θ with increments of 0.02° 2θ.

3.2.5 TEM-diffraction analysis

TEM samples were prepared by dispersion of the powder samples in high purity ethanol and sonicating for several minutes. Then a drop of sample solution was dropped onto a TEM grid. TEM-diffraction patterns were obtained using selected area electron diffraction (SAED) with a camera length of 340 mm and wave length of 0.0197.

3.2.6 X-ray absorption near edge structure (XANES)

X-ray absorption near edge structure (XANES) with the aid of linear combination fitting (LCF) was performed to investigate whether the chemical extractability of As(V) in soil changed with different Fe oxides. The XANES spectra of the Fe K-edge were collected from the beamline 10C at the Pohang Accelerator Laboratory (PAL) in South Korea. The samples were analyzed in transmittance mode using Fe foil as a reference. The edge-normalized spectra used for the LCF of the soil samples included three crystalline types of goethite (α-FeOOH), hematite (α-Fe_2O_3), and magnetite (Fe_3O_4), two amorphous kinds of ferrihydrite [$(Fe^{3+})_2O_3 \cdot 0.5H_2O$], and schwertmannite [$Fe_8O_8(OH)_6(SO_4) \cdot nH_2O$], and calcium iron arsenate types of arseniosiderite. The XANES spectra of the As K-edge were collected in fluorescence mode and calibrated with powder type of Na_2HAsO_4 as a reference. Also, samples of As(V) adsorbed onto or co-precipitated with various Fe oxides were used as predictor components for LCF analysis.

The goodness of the fitting was evaluated using R-factor and reduced Chi-square (χ^2). The R-factor is calculated as the sum of the squares of the difference between the fit and the data. Reduced χ 2 is the fitting metric divided by the number of degrees of freedom (Manning 2005). The LCF of the soil spectra were quantified using Athena software (Ravel and Newville 2005). The composition of each sample can be acquired through a combination of the predictors that have the smallest R-factor and reduced χ^2.

3.2.7 Co-precipitation of As(V) with Fe oxides

Co-precipitation sample (COP) was synthesized by inducing precipitation of ferrihydrite in As(V) solution. The sample was prepared by dissolving 40 g of $Fe(NO_3)_3 \cdot 9H_2O$ in 500 mL deionized water, adding 330 mL of 1 M KOH, and adjusting pH to 7-8. For adsorption sample (ADS), 1 g of Fe oxides was mixed with an appropriate amount of As(V) solution. Each sample was shaken at room temperature (180 rpm, 24 h). After the agitation, the sample was centrifuged at 10,000 g for 10 min. The precipitate was dried after washing three times with dH_2O.

3.2.8 *In situ* stabilization of As-contaminated soil

To induce *in situ* formation of amorphous Fe oxides, a powder of $Fe(NO_3)_3 \cdot 9H_2O$ was added to soil at 2% sample weight. Then, dH_2O was injected into soil samples at 30% L/S ratio, and pH was adjusted to neutral levels with NaOH. After vortex, the soil sample was allowed to react at room temperature for 24 h.

3.2.9 *In situ* stabilization using different type of neutralizing agents

① Synthesis of Fe oxides using neutralizing agents

COP sample was synthesized by simultaneously adding As(V) and the Fe(Ⅲ) solution, and adjusted pH to 7 using NaOH or CaO. The mixture was agitated at room temperature (180 rpm, 2 h). After the agitation, the sample was centrifuged at 10,000 g for 10 min The precipitate was then dried after washing three times with dH_2O.

② *In situ* stabilization using different type of neutralizing agents

Powder type of ferric nitrate was added to the As-contaminated soil at a weight of 2% and mixed with dH_2O (S/L ratio of 0.3 mg/L). Sample pH was adjusted to neutral levels using NaOH or CaO to induce formation of Fe oxides. Then, the soil sample was reacted at room temperature for 24 h. Fractionation of soil arsenic and bioaccessibility was assessed to compare the stabilization effects depending on type of the neutralizing agent.

③ Sample preparation for X-ray absorption spectroscopy (XAS)

For the XANES spectra of the Fe K-edge, various Fe oxides expected to be present in the soil were prepared. Ferrihydrite, schwertmannite, hematite, goethite and aseniosiderite were synthesized, while magnetite was used as a reagent (Daejung Chemical and Metals, Siheung, Korea). First, schwertmannite was prepared by adding 10.8 g of $FeCl_3 \cdot 6H_2O$ and 3 g of Na_2SO_4. The solution was hydrolyzed for further 12 min at 60 °C in the oil bath. After cooling to room temperature, the suspension was centrifuged at 10,000 g for 10 min, and then dried (Park et al. 2016). Hematite, a kind of crystalline Fe oxides, was synthesized from 2 L of 0.002 M HCL preheated to 98 °C with addition 16.6 g of $FeNO_3$. For goethite, 180 mL of 5 M KOH was added to 1 M $FeNO_3$ solution. The suspension was diluted to 2 L with dH_2O and heated to 70 ℃ for 60 h in the oil bath. Centrifuged suspension was washed with dH_2O several times and then dried in the oven (Schwertmann and Cornell

2000). Arseniosiderite, calcium iron arsenate, was prepared by mixing of 0.2 M $Ca(NO_3)_2$, 0.3 M $Fe(NO_3)_3 \cdot 9H_2O$, and 0.3 M As(V) and adjusting pH to 4-5 with NaOH. The mixture was stirred and placed at 85°C in the oil bath for 48 hours (Paktunc et al. 2015). For the As K-edge spectra, COP and ADS samples were prepared for various Fe oxides synthesized above.

3.3 Analytical method

3.3.1 ICP-OES

Heavy metal concentrations of the samples were analyzed by using inductively coupled plasma optical emission spectroscopy (iCAP 7400 ICP-OES, Thermo Fisher Scientific, USA). In ICP-OES, plasma energy makes the atoms excited which are target to analysis. When the atoms return to lower energy position, the emission rays or spectrum rays are released. By this, the emission rays that correspond to the photon wavelength can be measured. In order to generate plasma, sufficient argon gas should be supplied to torch coil, and high frequency electric current be applied to the work coil on the tip of the torch tube. When the electromagnetic field was created in the torch tube by the high frequency current, the plasma is generated as argon gas is ionized. At that time, high temperature (10000K) of the plasma is used to the excitation-emission of the sample to be analyzed. The solution sample is introduced into the plasma in the ionized state along the tube at the center of the torch tube (Fassel and Kniseley 1974).

Fig.3.1. iCAP 7400 DUO

3.3.2 X-ray absorption spectroscopy (XAS)

X-ray absorption spectroscopy (XAS) is an analytical method that can grasp structure by atomic unit. it include X-ray absorption near edge structures (XANES) and extended X-ray absorption fine sturcuters (EXAFS). In this study, XANES with the aid of linear combination fitting (LCF) was performed to investigate whether the chemical extractability of As(V) in soil changed with different Fe oxides. XANES is a technique for observing excited states of electrons trapped in an atom while changing the energy of the X-ray. When the energy near the ionization energy of a specific electron in an atom is irradiated with gradually increasing the energy of the X-ray, the electron absorbs the X-ray and transitions to vacancy of the higher state energy level. When the energy of the incoming X-ray is very high, the electrons move out of the atom and travel around the material and are scattered by near atoms, which affects the absorption spectrum. Therefore, the XANES spectrum measures the density of the outermost orbital electrons as a function of the energy of the local density of states (LODS) and also contains information about the local structure (Koningsberger and Prins 1988).

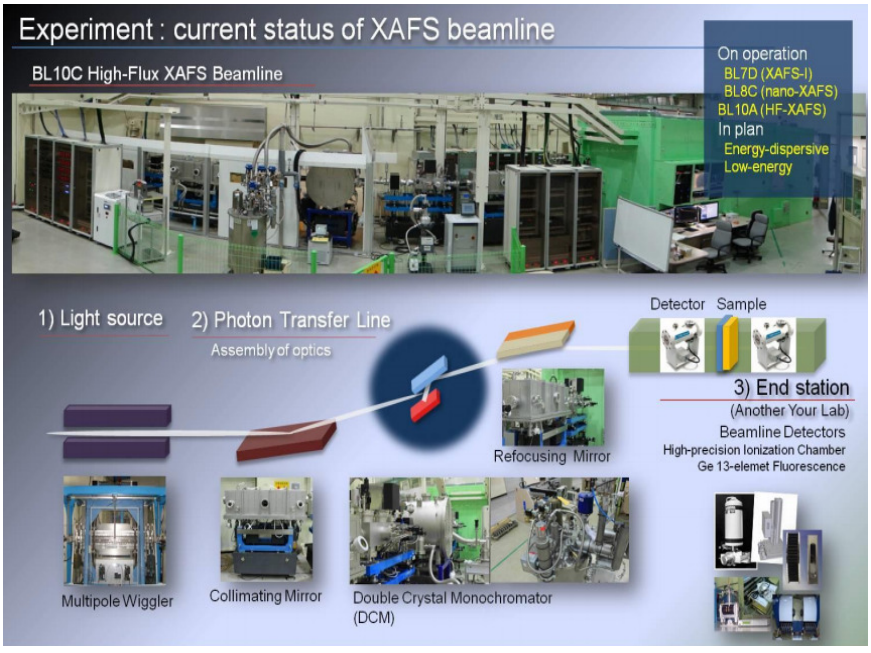

Fig.3.2. Beamline of Pohang Accelerator Laboratory (PAL) (Pohang Accelerator Laboratory 2019)

4. Results and discussion

4.1 Co-precipitation of Fe oxides

4.1.1. Confirmation of co-precipitation

Co-precipitation (COP) occurs when Fe oxides precipitates in the presence of As(V) in solution, while adsorption (ADS) does when added onto pre-formed Fe oxides. In this study, the concepts of co-precipitation are as follows. First, As(V) in solution can be inserted in during formation of Fe oxides. This means that As(V) may be present in the particle of Fe oxides. Also, since amorphous Fe oxides form aggregates at a rapid rate, As(V) can be trapped in the aggregates. Therefore, spectroscopic analysis was carried out to confirm co-precipitation of Fe oxides with As(V) in the solution in this chapter.

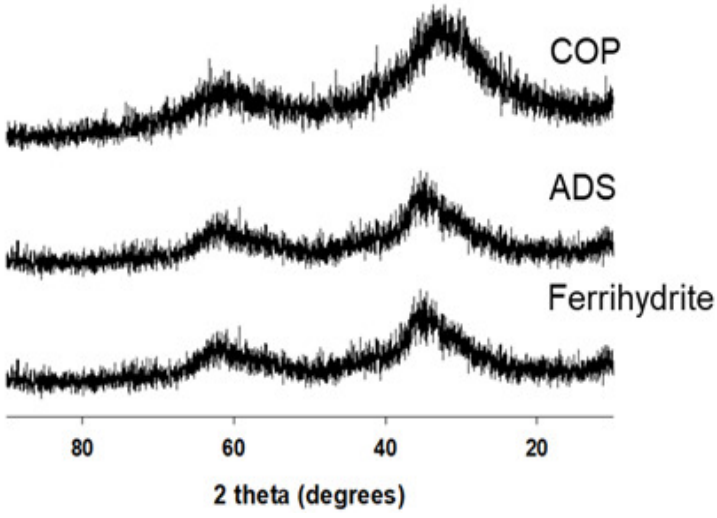

Fig.4.1. XRD pattern for synthetic ferrihydrite, As(V) adsorbed onto ferrihydrite (ADS), and co-precipitated As(V) with ferrihydrite (COP)

Firstly, XRD analysis was performed on the synthesized ferrihydrite, ADS sample and COP sample. Because the samples of As(V)-Fe oxides were synthesized at room temperature, they were poorly crystalline Fe oxides. Therefore, it was difficult to differentiate between the ADS sample and COP sample through powder XRD pattern. It was confirmed that both samples are amorphous Fe oxides similar to 2-line ferrihydrite, which shows two broad peak in XRD analysis. However, the synthetic ferrihydrite and ADS sample exhibited two broad characteristic XRD bands located at ~35° and ~61°2θ, whereas the characteristic XRD bands of COP sample at ~33° and ~61°2θ. In particular, decreased 2θ in COP sample indicates an increase in d-spacing due to expansion (i.e. distortion) of the lattice structure. Also, such different d-spacing between the samples was confirmed by TEM-diffraction analysis. The d-spacing of the COP sample was about 0.18 nm larger than ADS sample, based on the largest value obtained from TEM-diffraction. It also suggests that As(V) is occluded inside ferrihydrite particles in the COP sample, which may changed the structure of the particles.

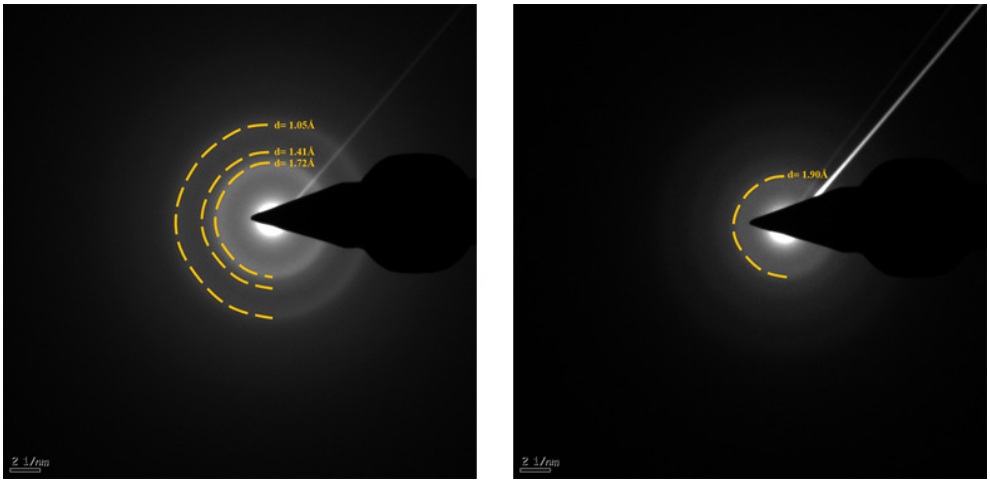

Fig.4.2. TEM-diffraction of ADS and COP sample

4.1.2. Assessment of bioaccessibility

In this study, bioaccessibility of As(V) was evaluated through the SBRC method, which quantifies the concentration of As(V) that can be absorbed under simulated human gastric conditions. At first, in COP samples, Fe concentration extracted by SBRC was 6.8 times more higher than ADS sample. On the other hand, concentration of extracted As(V) by SBRC test was 1.8 times lower in COP sample compared to ADS sample (Fig.4.3). These results indicate that co-precipitated As(V) with Fe oxides is resistant to SBRC test, meaning to have lower bioaccessibility than adsorption. Therefore, it is expected that bioaccessibility of As(V) can be lowered when As(V)-contaminated soil was stabilized by co-precipitation of Fe oxides.

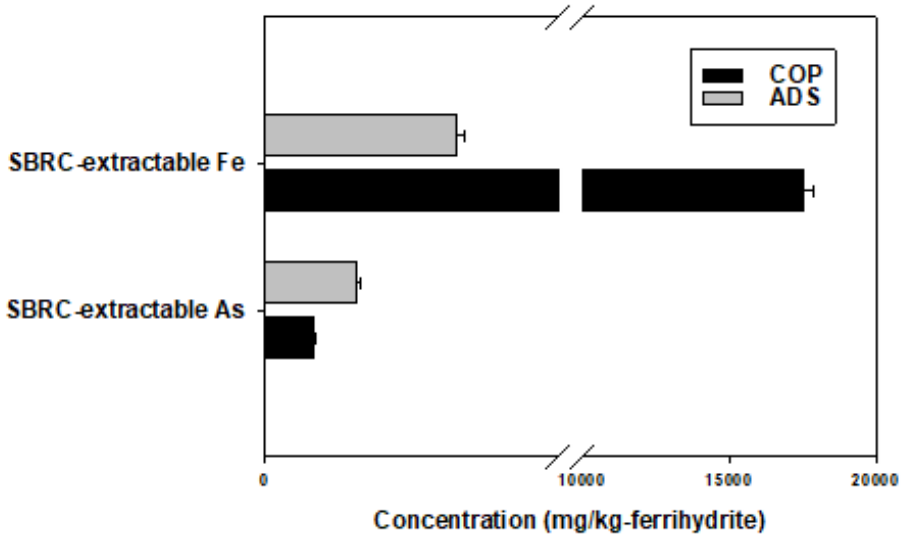

Fig.4.3. Concentration of Fe and As extracted by SBRC in ADS and COP samples

4.2 *In situ* stabilization of As-contaminated soil

4.2.1. Stabilization effect to As-contaminated soil

Formation of amorphous Fe oxides was carried out by injecting 2% of iron nitrate relative to the soil mass, and 30% water, and adjusting to neutral pH. In fact, iron nitrate was used to induce precipitation of amorphous Fe oxides, and to increase desorption of As(V) weakly bound to the soil. After addition of iron nitrate, pH was rapidly decreased and such acidic pH might have induced the change in species of non-specifically bound As(V). Therefore, chemical extraction and the bioaccessibility of As(V) in stabilized soil with iron nitrate were compared with those before stabilization. Bioaccessibility and chemical forms of As(V) were determined in freshly spiked soil samples by the SBRC method and the five step extraction, respectively.

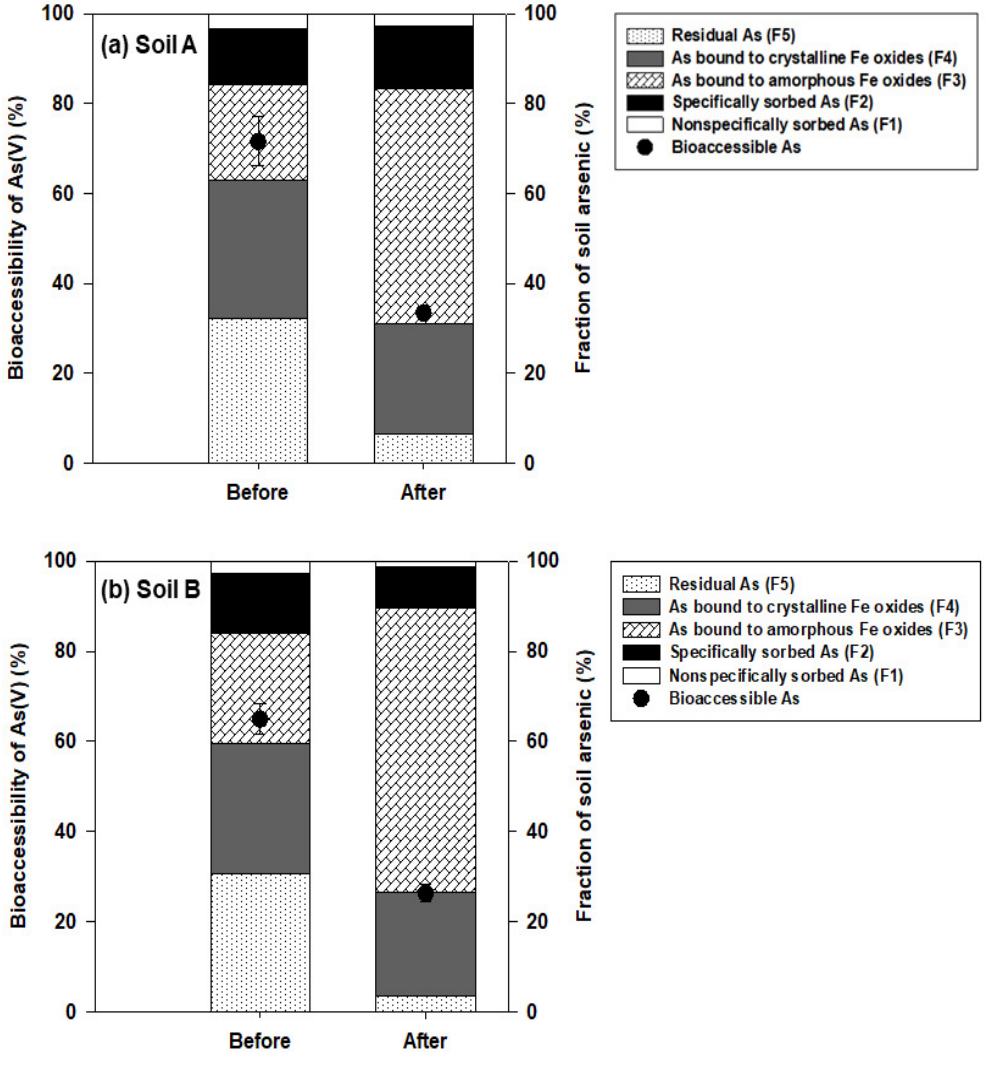

Fig.4.4. Bioaccessibility and chemical form of As(V) before and after *in situ* stabilization in freshly spiked soil A (a) and soil B (b)

After *in situ* formation of Fe oxides, bioaccessibility of As(V) in soil was greatly decreased from 71.6 to 33.5% and 64.9 to 26.3% in soils A and B, respectively. Consistent with the previous studies indicating that non-specifically and specifically bound As(V) corresponds to bioaccessible fraction in soil, the fraction of non-specifically bound As(V) was remarkably decreased in our study. In contrast, the method that we followed in this study to occur in *situ* Fe oxide synthesis generates amorphous Fe oxides and thus the As(V) fraction bound to amorphous Fe oxides was greatly increased by 2.4 and 2.6 times in soils A and B, respectively. And probably, this contributed to the reduction of bioaccessibility of soil As(V) from 71.6 to 33.5% and 64.9 to 26.3% in soil A and B, respectively (Fig.4.4). It is likely that amorphous Fe oxides is formed from the Fe-nitrate introduced during the stabilization process, and As(V) is co-precipitated while amorphous Fe oxides are newly formed in soil. This fraction of As(V) exhibits such low bioaccessibility since co-precipitation is more effective in reducing the bioaccessible As(V) than adsorption (Jeong et al. 2017).

4.2.2 Long-term stabilization effect

To investigate the long-term effectiveness of stabilization, *in situ* formation of Fe oxides was carried out in As-contaminated soil, and the soil samples were aged for five months. After aging, SBRC-extractable fractions (i.e., bioaccessible fraction) and chemical forms of As(V) were determined with the As-stabilized soils (Fig.4.5).

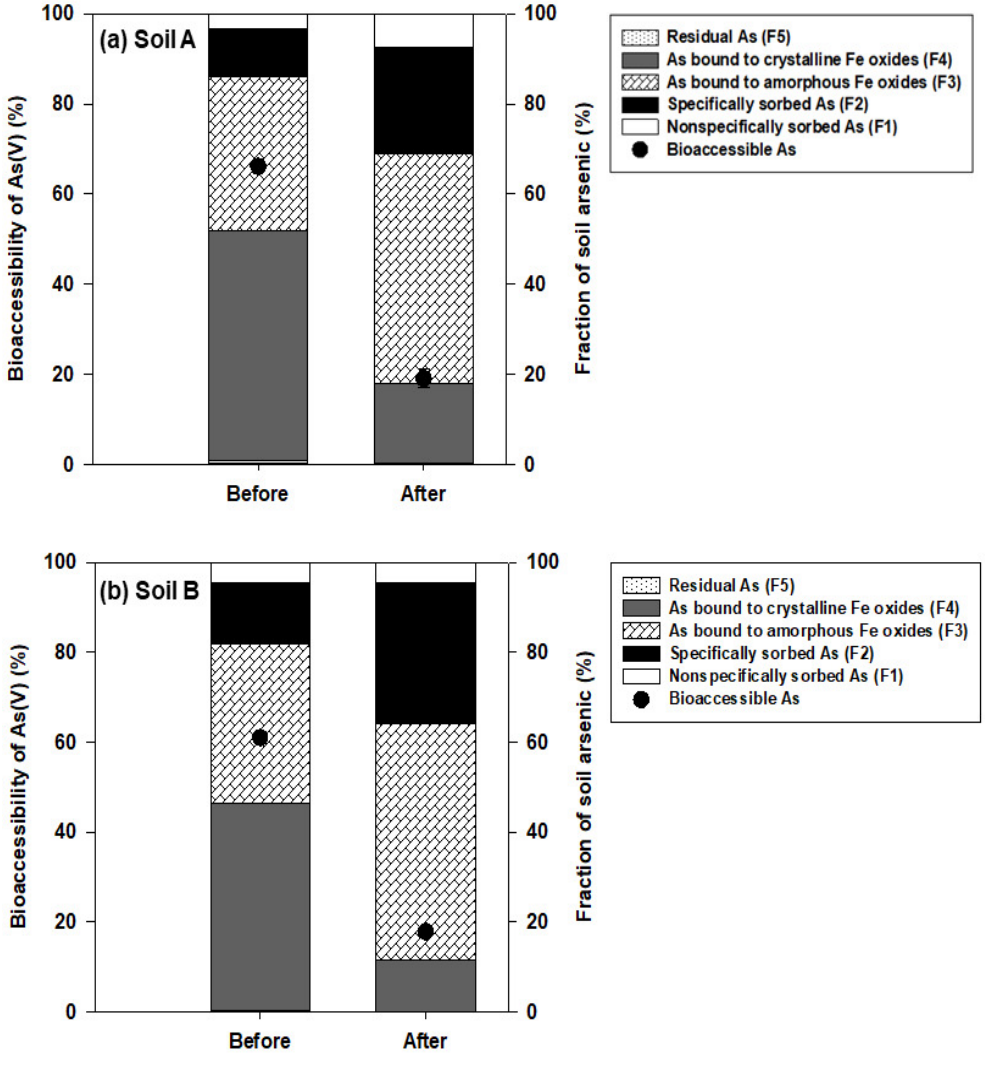

Fig.4.5. Bioaccessibility and chemical form of As(V) before and after *in situ* stabilization in five-months aging soil A (a) and soil B (b)

The percentages of bioaccessible As(V) in five months aged soils A and B without stabilization were 66.1 and 61.0%, respectively, however, reduction of bioaccessibility of As(V) was remarkable, showing 19.0 and 17.8% in the soils A and B, respectively which had been aged for five months after *in situ* stabilization. When comparing Fig.4.4 (a) and (b), it is evident that such decrease in bioaccessibility of soil As(V) was due to *in situ* synthesis of Fe oxides, not from aging itself. The reason can be ascribed to the harshness of SBRC extraction method used to represent oral bioaccessibility. The SBRC method uses a glycine-buffered solution with pH 1.5, and the soil particles less than 150 um in diameter are used for extraction. Such a harsh extraction condition seems to allow only the soil As(V) fractions that are co-precipitated or more tightly sorbed resist to SBRC extraction and thus became less bioaccessible.

Chemical forms of As(V) also differed before and after *in situ* stabilizaton in aged soils. It is noteworthy that the fraction of specifically bound As(V) dramatically decreased after stabilization process, which resulted in the remarkable increase of As(V) associated with amorphous and crystalline Fe oxides. More importantly, As(V) bound to crystalline Fe oxides dramatically increased from 9.0 to 23.5% and 14.0 to 31.2% in the five-months aged soils A and B, respectively that had been stabilized by *in situ* Fe oxides synthesis. Such increase in crystalline Fe oxides bound As(V) could be explained when assumed that some of the amorphous Fe oxides, newly precipitated by *in situ* stabilization, become crystallized with time. Indeed, it is previously reported that poorly ordered ferric oxyhydroxide minerals are often transformed to more thermodynamically stable minerals such as hematite or goethite

(Cudennec and Lecerf 2006). This was further proved by X-ray absorption spectroscopy in this study.

4.2.3. XANES analysis

In this study, XANES-LCF was performed to quantify the types of Fe oxides that are formed by *in situ* stabilization of As-contaminated soil. The LCF results for stabilized soils include Fe oxides generated from *in situ* stabilization. Two soil samples were analyzed. In the first, the original composition of the Fe oxides was magnetite (21.3%) and schwertmannite (78.7%). After stabilization, it changed to schwertmannite (81.6%), ferrihydrite (15.9%), and magnetite (2.5%). Since the total Fe oxide content increased after stabilization, the reduced fraction of magnetite in stabilized soil shows a relative ratio to other Fe oxides, not a quantitative decrease. As a result, ferrihydrite and schwertmannite, which are amorphous Fe oxides, quantitatively increased in the stabilized soil sample. In the second soil sample, the original composition was goethite (6.1%), magnetite (24.2%), and schwertmannite (69.7%), but changed to goethite (1%), magnetite (4.1%), and schwertmannite (94.9%) after stabilization. When quantified based on the approximate total Fe oxide contents, schwertmannite seems to have increased about 10 times after stabilization; however, goethite and magnetite did not notably decrease.

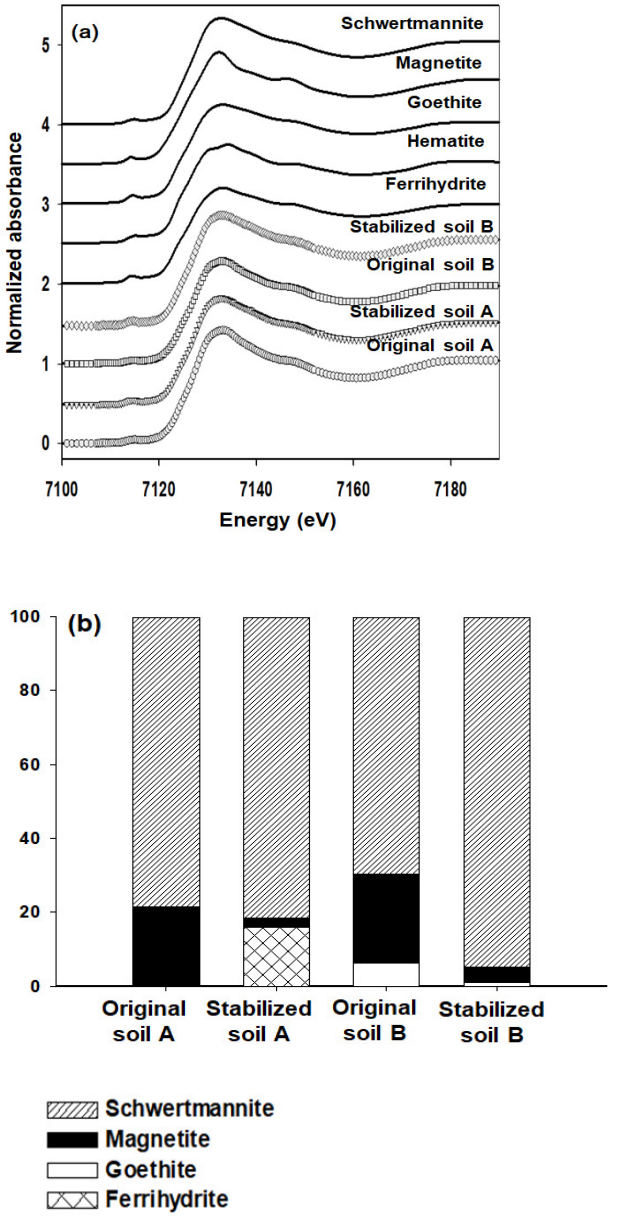

Fig.4.6. Fe K-edge XANES spectra of the original soils, stabilized soils, and reference materials (ferrihydrite, hematite, goethite, magnetite, and schwertmannite) (a) and linear combination fitting (LCF) results of the original soils, and stabilized soils (b)

Based on the LCF results, it was confirmed that amorphous Fe oxides such as ferrihydrite or schwertmannite could be generated when *in situ* stabilization was applied to As-contaminated soil (Fig.4.6). Therefore, the increase of As(V) bound to amorphous Fe oxides (F3) after stabilization seems to be the result of co-precipitation of soil As(V) with schwertmannite or ferrihydrite formed in stabilization process.

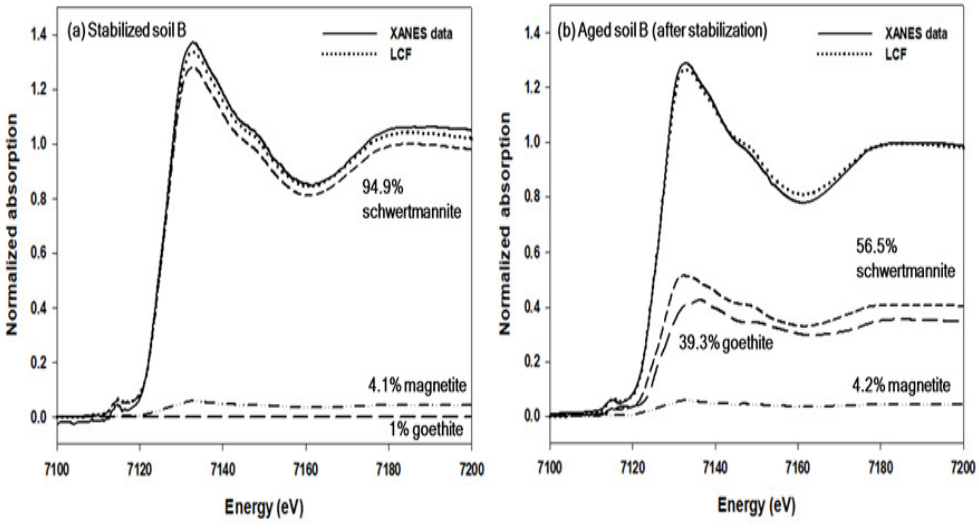

Fig.4.7. Fe K-edge XANES spectra and linear combination fitting (LCF) results of the freshly stabilized soil B (a) and aged soil B (after stabilization) (b)

In this study, XANES-LCF of aged soil (after stabilization) was performed to investigate how amorphous Fe oxides, which were formed by stabilization, changed over the long-term. After aging, schwertmannite decreased from 94.9 to 56.5% and goethite increased from 1.0 to 39.3%. There was no significant change in magnetite. Goethite has been known to be formed via recrystallization and drying of amorphous Fe oxides such as schwertmannite, which can be formed in the presence of high SO_4^{2-} concentrations (Park et al. 2016). Therefore, the increase of As(V) bound to crystalline Fe oxides (F4) in sequential extraction may be the result of transformation of schwertmannite to goethite through aging (Fig.4.7).

4.3 Effect of neutralizing agents

4.3.1. Effect on bioaccessibility

To confirm the effect of the neutralizing agents on bioaccessibility, SBRC was performed on Fe oxides synthesized using two type of neutralizing agents. As the result, bioaccessibility was much lower in that case of being synthesized with NaOH than CaO (Fig.4.8). In previous study, it is reported that Ca-Fe arsenate minerals have high bioaccessibility (Whitacre et al. 2017).

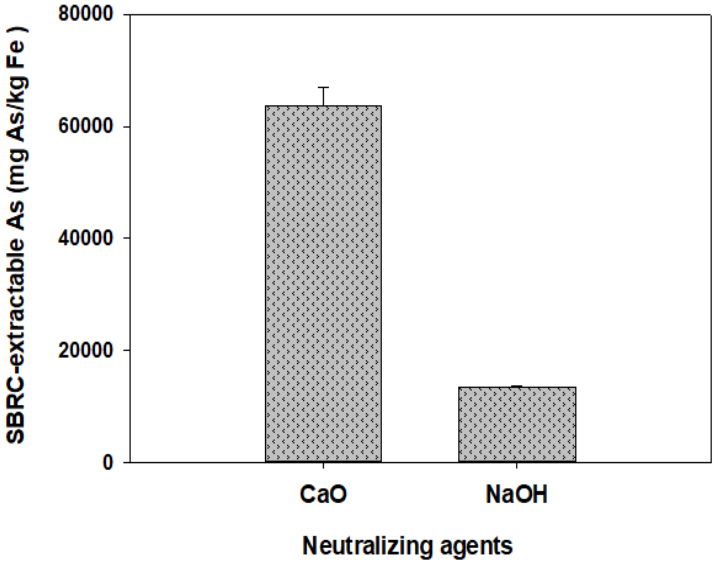

Fig.4.8 As(V) concentration extracted by SBRC methods from Fe oxides that was synthesized by using different neutralizing agents

4.3.2. Effect on stabilization of As-contaminated soil

In a sandy loam with 1,035 mg-As/kg (i.e. soil C), *in situ* stabilization was carried out by 2% iron nitrate and using CaO or NaOH as neutralizing agents. The liquid-to-solid (L/S) ratio was 0.3 g/L. A five-step sequential extraction suggested by Wenzel et al. was conducted to compare the chemical forms of As(V) in soil after *in situ* stabilization depending on the type of neutralizing agents. Fraction of soil As(V) and bioaccessibility were shown in percentage (Fig.4.9)

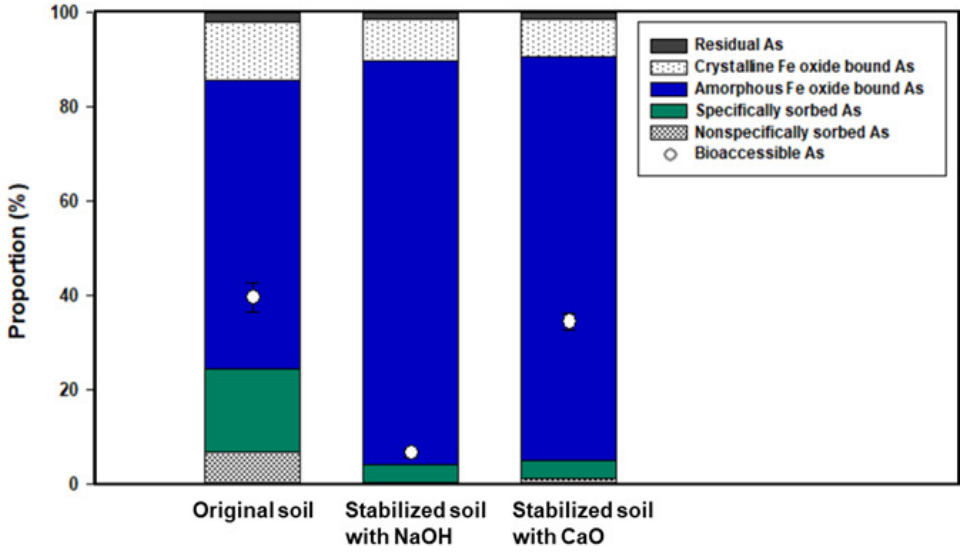

Fig.4.9 Changes of chemical forms and bioaccessibility in soil As(V) before and after *in situ* stabilization depending on different type of neutralizing agents

After *in situ* stabilization, the fraction of non-specifically and specifically bound As(V) was remarkably decreased in both samples. On the other hand, As(V) bound to amorphous Fe oxides increased from 61.2% to 85.4% and to 85.5% in the stabilized soil with CaO and in the stabilized soil NaOH, respectively. In particular, it is noteworthy that the fraction of As(V) bound to amorphous Fe oxides was no significantly different in both samples, however, bioaccessibility were differed. Bioaccessibility was remarkably decreased by 83% in only soil stabilized with NaOH, while was not in the soil stabilized with CaO. Meunier et al (2010) reported that soil amendments such as liming may increase bioaccessibility of As(V), because labile calcium on neutral pH may effects on formation of calcium-iron arsenate which has high bioaccessibility. Such high bioaccessibility in soil stabilized with CaO could be explained when confirmed that some of calcium-iron arsenate was formed after *in situ* stabilization. This was further proved by X-ray absorption spectroscopy in this study.

4.3.3 XANES analysis

In this study, XANES-LCF was performed to quantify the types of Fe oxides that are formed by *in situ* stabilization of As-contaminated soil. The LCF results for stabilized soils include Fe oxides generated from in situ stabilization. Fe K-dege XANES spectra of soils before and after *in situ* stabilization were compared with the XANES spectra of several synthesized Fe oxides (i.e., magnetite, ferrihydrite, schwertmannite, and arseniosiderite). The linear combination fitting of XANES spectra for soil was estimated by the spectrum of Fe oxides

(Fig.4.10.a), and the composition changes in the soil are shown in Fig.4.10.b. The goodness of fitness determined by an R-factor of 0.0094 and a reduced χ^2 of 0.0031 in the original soil, and 0.0069 and 0.0019 in the stabilized soil with NaOH, and 0.0044 and 0.0012 in the stabilized soil with CaO, respectively.

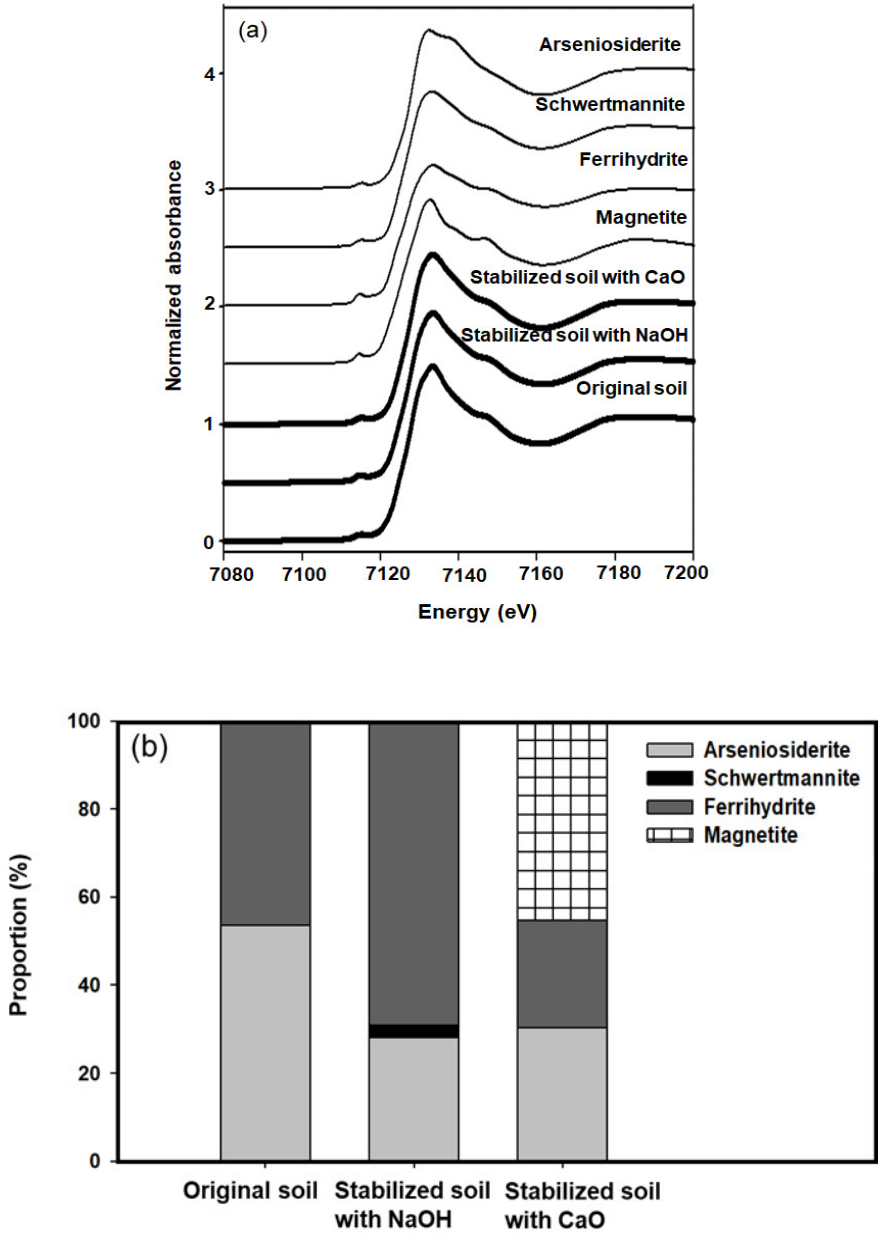

Fig.4.10 Iron K-edge XANES spectra of the original soil, stabilized soil with NaOH, stabilized soil with CaO, magnetite, ferrihydrite, schwertmannite, and arseniosiderite (a) and linear combination fitting (LCF) results of the original soil and the stabilized soils with NaOH and CaO (b)

In the first, the original composition of the Fe oxides was magnetite (53.6%) and schwertmannite (46.4%). After stabilization with NaOH, it changed to magnetite (28%), ferrihydrite (2.9%), and schwertmannite (24.4%). Since the total Fe oxide content increased after stabilization, the fraction of Fe oxides in stabilized soil shows a relative ratio to other Fe oxides not a quantitative ratio. Therefore, ferrihydrite and schwertmannite, which are amorphous Fe oxides, quantitatively increased in the stabilized soil. On the other hands, it changed to magnetite (30.4%), schwertmannite (24.4%) and arseniosiderite (45.2%) after stabilization with CaO. Based on the LCF results, it was confirmed that amorphous Fe oxides such as ferrihydrite or shcwertmannite could be generated when NaOH was used as neutralizing agent, while arseniosiderite (i.e., a kind of calcium iron arsenate) was formed when CaO used.

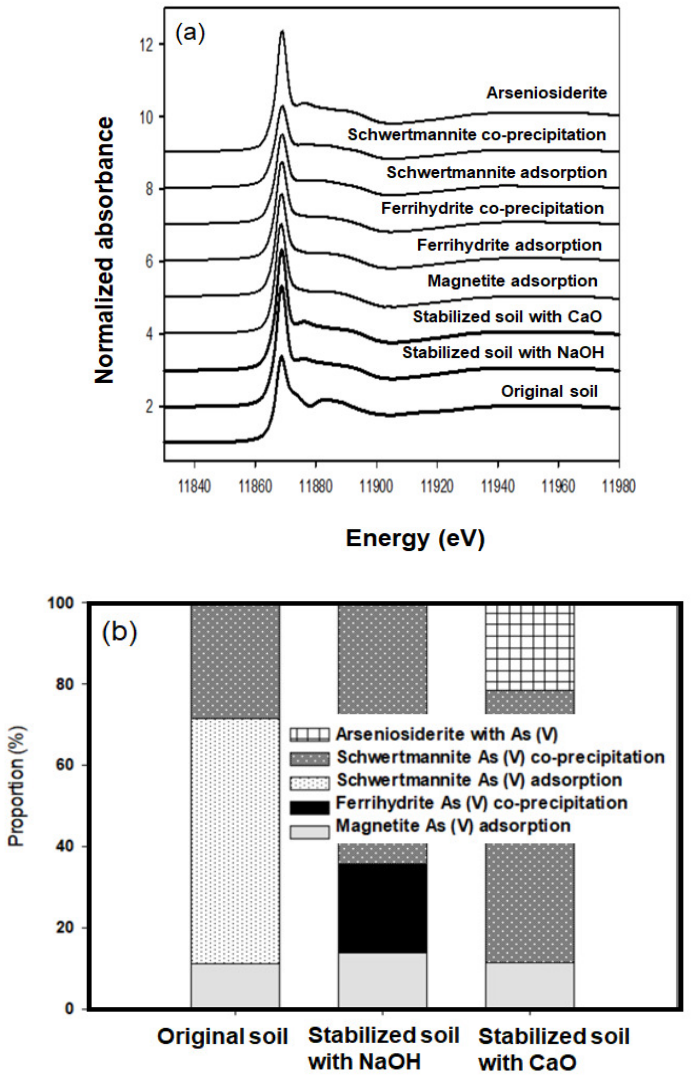

Fig.4.11 Arsenic K-edge XANES spectra of the original soil, stabilized soil with NaOH, stabilized soil with CaO, magnetite As(V) adsorption, ferrihydrite As(V) co-precipitation, schwertmannite As(V) adsorption, schwertmannite As(V) co-precipitation, and arseniosiderite (a) and linear combination fitting (LCF) results of the original soil and the stabilized soils with NaOH and CaO (b).

As K-edge XANES spectra of the soils were presented in Fig. 4.11 with several Fe oxides incorporated with As(V) (i.e., magnetite, ferrihydrite, schwertmannite, and arseniosiderite). The goodness of fitness determined by an R-factor of 0.0078 and a reduced χ^2 of 0.0055 in the original soil, and 0.0043 and 0.0028 in the stabilized soil with NaOH, and 0.0064 and 0.0029 in the stabilized soil with CaO, respectively. In the original soil, As(V) was adsorbed onto schwertmannite (60.4%), adsorbed onto magnetite (11.2%), and co-precipitated with schwertmannite (28.4%). After stabilization with NaOH, it changed to be adsorbed onto magnetite (13.7%.), co-precipitated with schwertmannite (64.3%) and ferrihydrite (22%). After stabilization with CaO, it changed to be adsorbed onto magnetite (11.3%), co-precipitated with schwertmannite (67.2%) and arseniosiderite (21.5%). Based on LCF results, As(V) co-precipitated with amorphous Fe oxides seems to have increased in both stabilized soils, while As(V) adsorbed onto Fe oxides decreased. However, despite the increase in As(V) co-precipitated with schwertmannite, the reason why the bioaccessibility of stabilized soils with CaO did not decrease is that As(V) bearing arseniosiderite is easily extractable by SBRC method. This result is consistent with high bioaccessibility of As(V) co-precipitated with Fe oxides synthesized by using CaO as a neutralizing agent.

5. Conclusions

In this study, *in situ* stabilization method was carried out to reduce bioaccessibility As(V) in soil through co-precipitation of amorphous Fe oxides. In addition, a method to improve the stabilization efficiency

was applied and verified. The results from this study are summarized as follows.

(1) *In situ* stabilization of As-contaminated soil in this study has the potential to massively reduce the bioaccessiblity of harmful environmental As(V). In situ stabilization was performed through the co-precipitation of amorphous Fe oxides and As. The formation of these Fe oxides was induced by injecting 2% soil mass of iron nitrate and 30% water, after adjusting the pH to neutral levels. The effectiveness of stabilization was assessed using chemical extraction, specifically sequential extraction and SBRC methods. With stabilization, the amorphous Fe oxides bound to As (F3) increased, and SBRC-extractable As decreased in all stabilized soils; this process seems to significantly decrease the risk of harm to humans through oral ingestion. Generally, conventional heavy metal and/or metalloid stabilization and immobilization has a short-term effect because the metals still remain in contaminated soil. In this study, however, crystalline Fe oxides bound to As (F4) increased, and the bioaccessibility of As decreased further in aged soils. Using XANES-LCF, we confirmed that amorphous Fe oxides formed during stabilization may gradually transform into crystalline Fe oxides. The LCF results suggest that the decrease in bioavailable As in stabilized soils over time is due to the crystallization of amorphous Fe oxides into a more stable form. Such results also show that *in situ* stabilization of As-contaminated soil is a viable approach and can be applied to reduce the bioaccessibility of arsenic contaminants and decrease risks to human health.

(2) In order to compare the effects of neutralizing agents on bioaccessiblity, soil pH was controlled by NaOH or CaO and induced *in situ* synthesis of Fe oxides. As a result of Wenzel sequential extraction, the amount of As(V) bound to amorphous Fe oxides increased regardless of the type of neutralizing agents. Bioaccessibility determined by SBRC method was not significantly decreased in stabilized soil with CaO (39.4%), however, it was significantly decreased by 5 times more when stabilized with NaOH. According to the result of XANES-LCF, amorphous Fe oxides (i.e. schwertamannite and ferrihydrite) were formed in NaOH treated soil, while calcium iron arsenate such as arseniosiderite did in CaO treated soil. Thus, it is important to stabilize As(V) in soil through co-precipitation with Fe oxides that is high tolerable to SBRC test, not calcium iron arsenates, which are known to have high bioaccessibility.

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초록

비정질 철산화물 원위치 공침을 통한 비소오염토양 안정화 및 생물학적접근성 저감

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본 연구에서는 토양 내 존재하는 비소를 보다 화학적 추출성이 낮은 형태로 안정화시키기 위하여 토양 내에서 비소와 공침할 수 있는 비정질 철산화물의 형성을 유도하였다. 원위치 조건에서 비정질 철산화물을 합성하기 위해 토양 질량 대비 2%의 질산철과 30%의 수분을 주입하고 pH는 중성수준으로 조절하였다. 안정화 전후 토양을 대상으로 5단계 연속추출을 수행한 결과 원래 토양에서는 쉽게 추출될 수 있는 형태로 존재하고 있던 비소의 50% 이상이 안정화 이후 감소하고 화학적으로 추출되기 어려운 형태의 비소로 변화되었다. 뿐만 아니라 안정화 이후 비소의 생물학적접근성 또한 크게 감소된 것으로 나타났다. 안정화 전 두 종류의 토양시료에서 확인된 비소의 생물학적접근성은 71.6%와 64.9%였으나 안정화 후에 각각 33.5%와 26.3%로 크게 감소하였다. 또한 XANES-LCF를 통해 확인한 결과, 안정화 된 토양에서는 schwertmannite 또는 ferrihydrite와 같은 비정질 철산화물이 형성되는 것으로 나타났다. 또한 이러한 안정화 효과가 오랫동안 유지될 수 있는지 확인하기 위해 5달 동안 상온에서 에이징시킨 안정화 후 토양을 대상으로 화학적 추출가능성과 생물학적접근성을 평가하였다. 연속추출 결과,

비정질 철산화물과 결합하고 있던 비소와 비소의 생물학적접근성은 감소하였으나 오히려 결정질 철산화물과 결합한 비소는 증가한 것을 확인할 수 있었다. 이는 안정화 후 에이징시킨 토양에서 결정질 철산화물인 goethite의 비율이 증가한 것으로 나타난 XANES-LCF 결과와 상응한다. 따라서 비정질 철산화물과의 공침을 통해 비소오염토양을 안정화시키는 경우 효과적으로 비소의 생물학적접근성이 감소할 뿐만 아니라 에이징 후 비정질 철산화물이 점차 결정질 철산화물로 결정화됨에 따라 안정화 효과가 장기적으로 유지될 수 있다는 것이 확인되었다.

또한 생물학적접근성의 측면에서 안정화 과정에서 사용되는 중화제가 미치는 영향을 확인해보기 위하여 두 종류의 중화제(CaO와 NaOH)를 사용하여 용액 상에서 비정질 철산화물을 합성한 후 SBRC 방법을 통해 각 시료의 생물학적접근성을 평가하였다. 그 결과 CaO를 중화제로 사용하여 공침시킨 철산화물보다 NaOH를 중화제로 사용한 시료에서 비소의 생물학적접근성이 더 낮은 것으로 확인되었다. 실제로 calcium iron arsenate는 높은 생물학적접근성을 갖는다는 연구결과가 보고된 바 있다. 이에 중화제가 실제 비소오염토양의 안정화에 미치는 영향을 확인하기 위하여 중화제의 종류를 다르게 한 후 동일한 방법으로 원위치 안정화를 수행하였다. 그 결과 안정화 후 토양에서는 중화제의 종류에 관계없이 비특이적, 특이적으로 결합된 비소의 비율이 크게 감소한 것을 확인할 수 있었다. 비정질 철산화물에 결합한 비소 또한 안정화 전 61.2%에서 NaOH를 사용한 경우 85.5%로, CaO를 사용한 경우 85.4%로 증가하여 중화제의 종류에 관계없이 비슷한 변화를 보였다. 그러나 NaOH를 중화제로 사용하여 안정화시킨 토양에서만 비소의 생물학적접근성이 크게 감소되었고, CaO를 중화제로 사용한 경우에는 안정화 전 토양과 비교하여 생물학적접근성이 비슷한 수준으로 유지되었다. 이는 철산화물 공침과정에서 중화제로 사용된 CaO로 인해 생물학적접근성이 높은 것으로 알려져 있는 calcium-iron arsenate가 형성되었기 때문이라고 판단되었다. 이를 확인하기 위해 XANES 분석을 수행한 결과, CaO를 중화제

로 사용하여 안정화시킨 토양에서만 calcium iron arsenate의 일종인 arseniosiderite가 형성되었음이 확인되었다. 이처럼 CaO를 중화제로 사용하여 비소오염토양을 안정화시키는 경우 생물학적접근성이 높은 calcium iron arsenate가 형성될 수 있으므로 철산화물 공침을 통한 비소오염토양의 안정화 시 적절한 중화제를 사용하여 생물학적접근성이 낮은 형태로 토양 내 비소를 안정화시키는 것이 중요하다고 할 수 있다.

주요어: 원위치 안정화, 비정질 철산화물, 생물학적접근성, 중화제, 제인스, 에이징

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